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LETTERS  
TO THE EDITOR

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*Dedicated to V. F. Mironov on His 60th Anniversary*

## Supramolecular Polymer Based on Aminated Monosubstituted Pillar[5]arene

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**Abstract**—The interaction of nonamethoxypillar[5]arene containing an ester fragment with a series of di- and triamines has yielded novel macrocyclic amide derivatives of pillar[5]arene. The data of NOESY  $^1\text{H}$ – $^1\text{H}$  and DOSY NMR spectroscopy, dynamic light scattering, and transmission electron microscopy have revealed that nonamethoxypillar[5]arene containing diethylenediaminoamide moiety can form a network supramolecular polymer with average pores size of 100 nm.

**Keywords:** pillar[5]arene, *N*-(2-aminoethyl-1,2-ethanediamine), ethylenediamine, tris(2-aminoethyl)amine, synthesis, macrocycle, supramolecular polymer

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Supramolecular systems involved in various dynamic processes and capable of the self-assembly have recently attracted much attention [1–4]. Due to the predefined properties and relatively good synthetic availability, such structures can be used for the preparation of materials with target properties [5–11]. Supramolecular polymers combining the features of supramolecular and high-molecular compounds are formed via the self-assembly of low-molecular monomeric building blocks via reversible noncovalent interactions are examples of such systems [1]. Derivatives of a novel class of macrocyclic compounds, pillar[*n*]arenes, have been recently recognized as convenient and synthetically available monomers [12–15]. Development of the approaches for the preparation of supramolecular polymeric structures containing monosubstituted pillar[5]arene fragments is a comprehensive issue which, when resolved, opens the way for the construction of “smart” materials reacting on the changes of the external medium (temperature, polarity, or pH) [16–18].

We chose derivative **2** (convenient for the introduction of polar linear substituents capable of the formation of the inclusion complexes as pseudo rotaxanes) as the starting material for the preparation

of precursors of monosubstituted pillar[5]arenes. A series of primary di- and triamines: *N*-(2-aminoethyl-1,2-ethanediamine), ethylenediamine, and tris(2-aminoethyl)amine were used as the mentioned substituents.

At the first stage, monohydroxylated pillar[5]arene **1** was transformed into the ethoxycarbonyl derivative **2** [19]. Then, aminolysis of macrocycle **2** with the corresponding di-, tri, and tetraamines in a toluene–methanol mixture afforded of the target products **3–5** in 67–85% yield (Scheme 1). The reaction was performed in the boiling mixed solvent during 48 h. The reaction progress was monitored by means of TLC. Structure and composition of the prepared compounds **3–5** was confirmed by the physical and physicochemical data: IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$ – $^1\text{H}$  NOESY spectroscopy, mass spectrometry, and elemental analysis.

To evaluate the possibility of self-assembly of compounds **3–5**, we recorded the spectra of macrocycles **3–5** in two solvents: DMSO- $d_6$  and  $\text{CDCl}_3$ . In the cases of compounds **3** and **5**, the  $^1\text{H}$  NMR spectra were similar. For example, the  $^1\text{H}$ – $^1\text{H}$  NOESY NMR spectrum contained no cross-peaks of the protons of amino ( $\text{H}^8$ ) and methylene ( $\text{H}^7$  and  $\text{H}^6$ ) groups with the protons of aromatic fragments ( $\text{H}^3$ ), evidencing no incorporation of the substituent fragments in the void